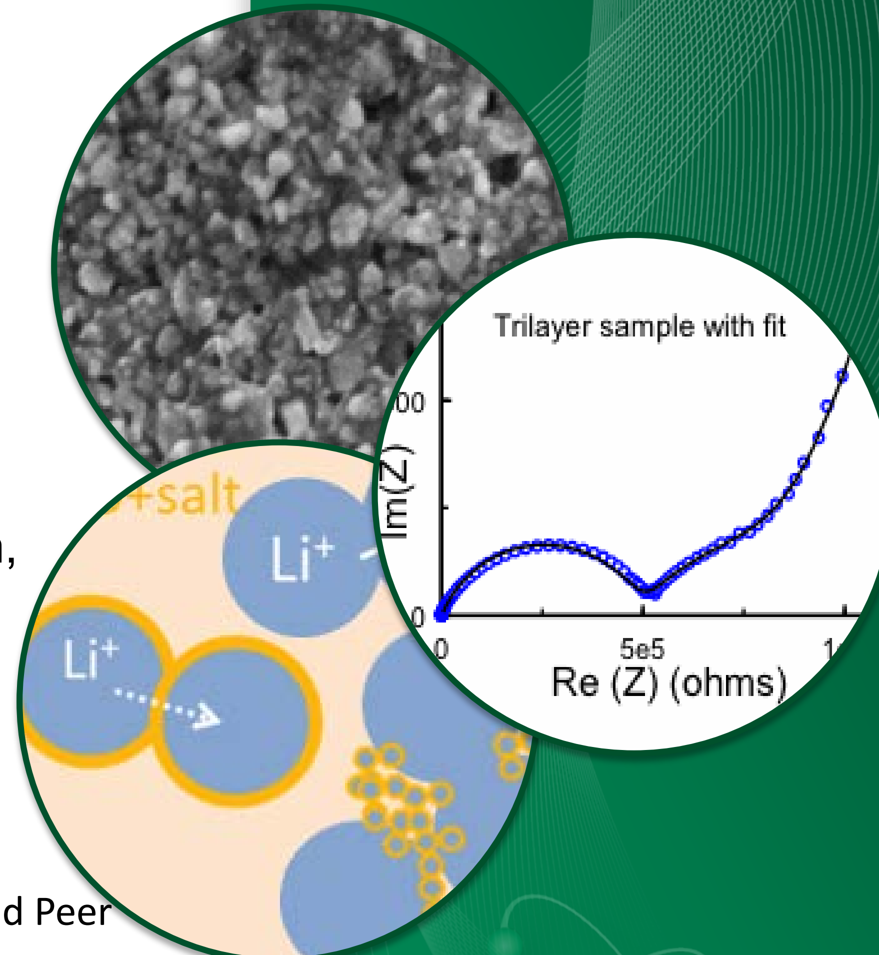
Composite Electrolyte to Stabilize Metallic Lithium Anodes



Project ID: ES273

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Material Science and Technology Division

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

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"This presentation does not contain any proprietary, confidential, or otherwise restricted information"

Overview – Composite Electrolytes to Stabilize Li Metal Anode

- **Timeline**
  - Start: October 2014
  - End: September 2018
- **Budget**
  - $400k FY16
  - $400k FY17
- **Technical barriers**
  - Energy density (500-700 Wh/kg)
  - Cycle life, 3000 to 5000 deep discharge cycles
  - Safety
- **Partners and collaborators**
  - Oak Ridge National Laboratory (lead)
  - Center for Nanophase Materials Sciences, ORNL
  - Collaborators:
    - Jeff Sakamoto, Michigan State University
    - Ohara Corporation, CA

To match Li-ion cathodes,	Li cycling must achieve:
20-40 μm Li per cycle	no loss to reaction
10-20 nm/sec, pulse	no loss to physical isolation
3000 cycles	no roughening or dendrites

STRATEGY

For high energy density, there can be no excess lithium in battery. Cycling of lithium must be stabilized by the solid electrolyte.

To match Li-ion cathodes and meet EV goals:

20^+ µm Li per cycle		no Li roughening
10-20 nm/sec, pulse	10-15 mA/cm^2, pulse	no Li lost to physical isolation
3000 cycles	99.99% coul. efficiency	no Li lost to reaction

What single solid has:
adequate Li$^+$ conductivity **AND**
robust mechanical properties **AND**
thin sheet processing **AND**
no pathways for dendrites **AND**
chemical stability with Li
?

→ composite of solid electrolytes

Can polymer-ceramic composite electrolytes protect the Li?

RELEVANCE

- **Objectives:**
  - Identify model polymer and ceramic electrolyte that are compatible to complement each other and deliver reasonable properties for working in a battery.
  - Identify a method for producing highly reproducible composite electrolyte.
  - Introduce a barrier layer between composite and lithium and understand the interface through different layers.
  - Fabricate a working battery to demonstrate the composite electrolyte.
  - Extend the design rules obtained to next generation of ceramic and polymer electrolytes.
- **Relevance to technical barriers:**
  - Multi-year program plan identifies the Li metal anode and its poor cycling as the fundamental problem for very high energy Li batteries. Using a solid electrolyte to isolate lithium from all liquid components is the best route to safety and efficiency.
  - Success of our composite electrolyte will:
    - Enable Li-S Battery (500 Wh/kg) by 2020 and Li-Air (700 Wh/kg) by 2030.
    - Fully protect lithium anode for long cycle life (3000 to 5000 deep discharge cycles).
    - Ensure lithium remains dense and free of dendrites (Safety).
    - Improve energy density lithium batteries (USABC has targeted a 5X improvement).

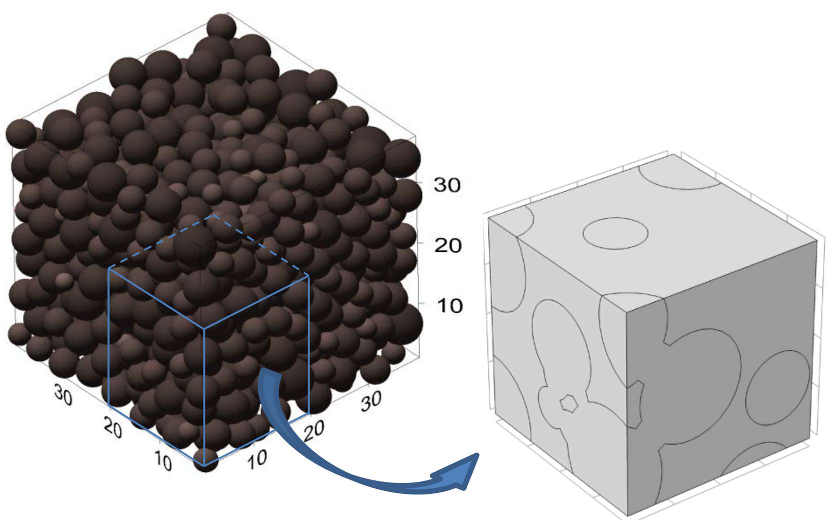
Milestones

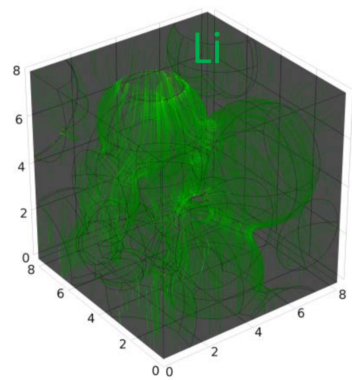
Milestones: FY16-FY17	Target:	Status:
Measure the removal of solvent molecules introduced via solution synthesis or gas absorption from ceramic-polymer composite sheets under vacuum and heating conditions.	Q1 FY16	
Prepare ceramic-polymer electrolyte sheets with a coating and map the uniformity with nanoindentation and by profile the Li plating.	Q3 FY16	Coated, alt. evaluation
For spray coated composites with high ceramic loading, vary the salt, plasticizer and ceramic content to achieve facile ion transport across phase boundaries and 10^{-5} S/cm.	Q2 FY17	Done, but shy of 10^{-5}
Assess the Li/solid electrolyte interface resistance. Adjust the composition and/or add a coating to reduce the ASR and passivate the interface.	Q3 FY17	On schedule, Initiated for baseline ASR
Fabricate a full battery using aqueous spray coating for both the composite electrolyte and cathode incorporating a protected Li metal anode. Demonstrate Li cycleability. (stretch goal)	Q4 FY17	On schedule

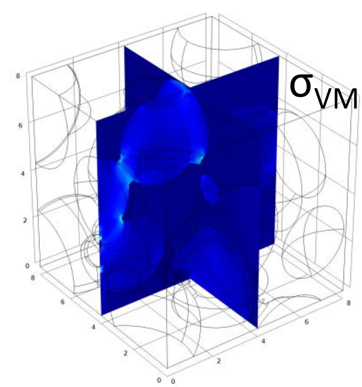
Background for approach: composite that is largely ceramic, with just enough polymer –

APPROACH

- Earlier models of modulus and conductivity of composites provided guidance for composition and structure goals (Kalnaus, this program)
  - High ceramic loading needed for high modulus in dispersed system.
  - Polymer-ceramic interface resistance is critical in dispersed composite.
  - Partial sintering so that necks connect ceramic particles eliminates need for highly conductive polymer electrolyte.
- Yet polymer electrolyte will facilitate manufacturing and handling.



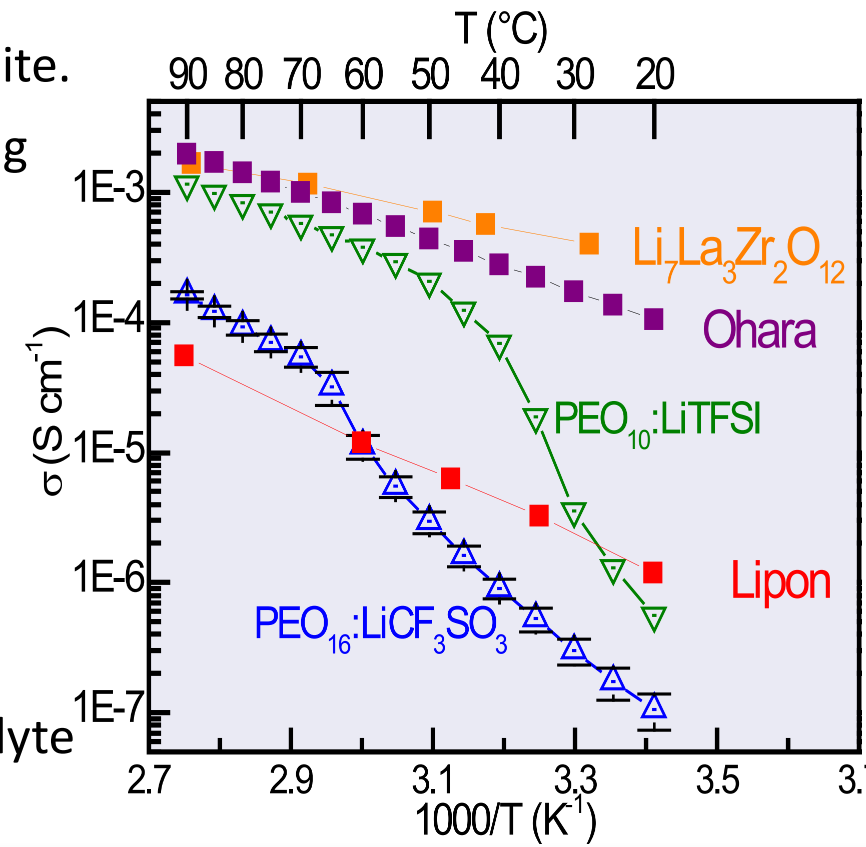




- Li transport through ceramics percolation network
- High stiffness with polymer providing additional cohesion

Use model electrolyte materials to develop processing

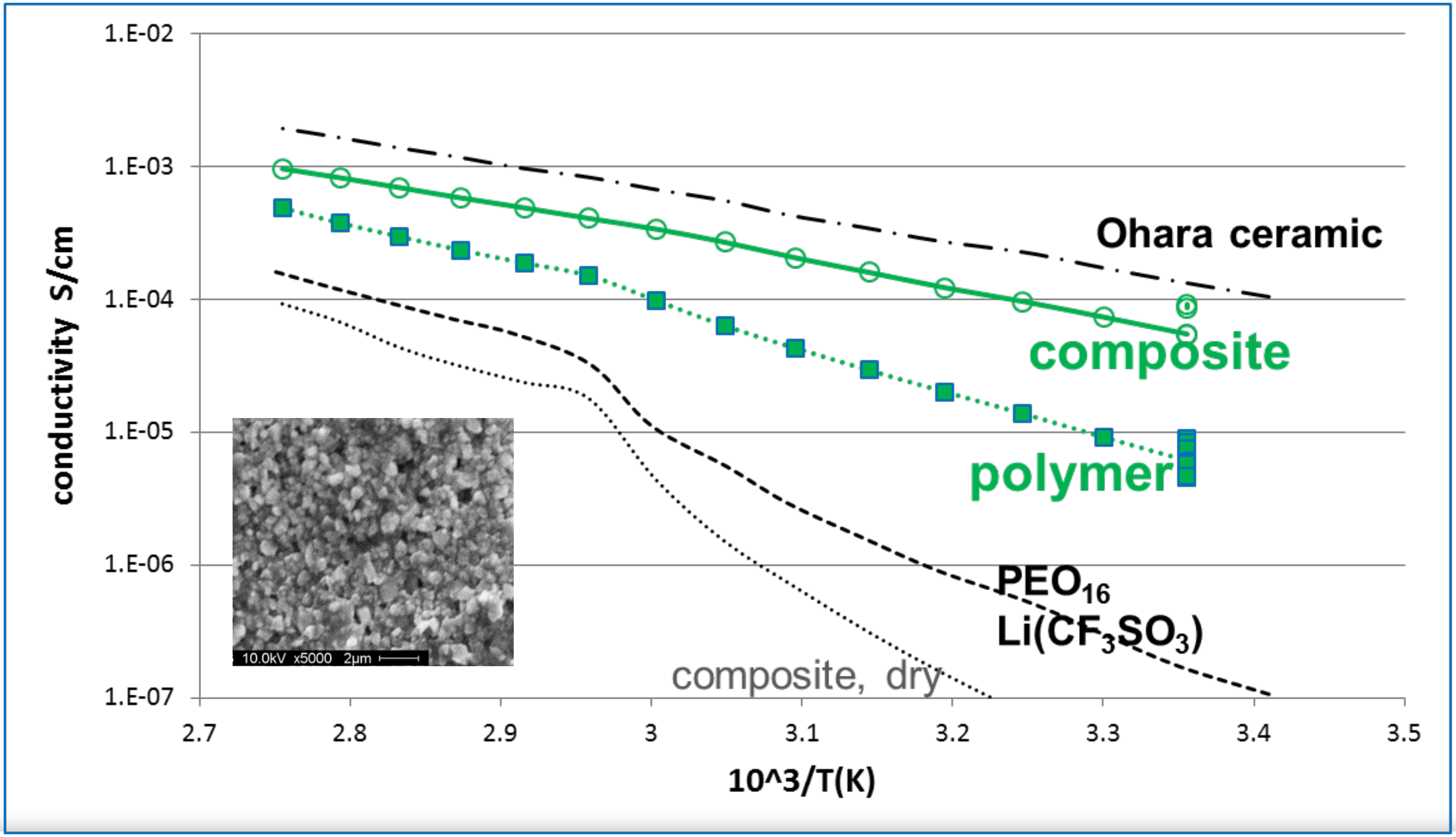
- **Model materials** used for study, which are already well understood, but maybe not the final choice:
  - PEO polymer with LiTriflate salt. Stable with Li; fast crystallization kinetics.
  - Ohara LATP based ceramic powders. Reproducible batch to batch, submicron powders. Air stable, but expected to reduce with Li contact.
- **Processing** for uniform, dense composite.
  - Target is much higher ceramic loading than other programs to produce mechanically strong membrane.
- **Characterization - electrochemical and mechanical**
  - Compare dispersed composite electrolytes with laminated polymer/ceramic samples.
- **Outcome –** Design rules that can be applied to alternative composite electrolyte materials and architectures.



Key earlier technical accomplishment: This works

EARLIER RESULT

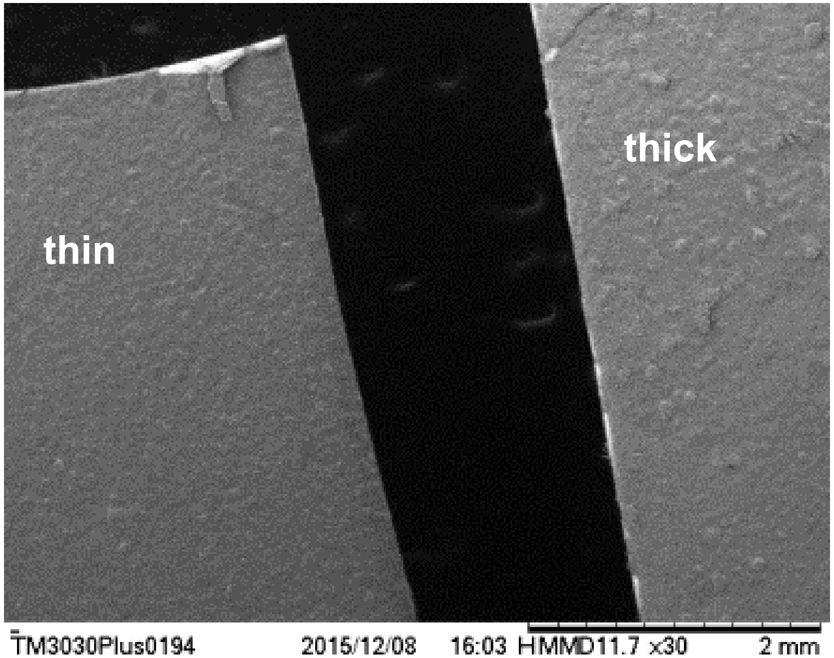
- Melt processed composites of PEO + Li triflate + 50 vol% Ohara ceramic powder conductive, ***if*** DMC is added by adsorption of vapor.
- Composite is stiff due to high vol.% ceramic.
- **Problems: DMC reacts with Li and evaporates. Hot pressing is not easily scaled.**

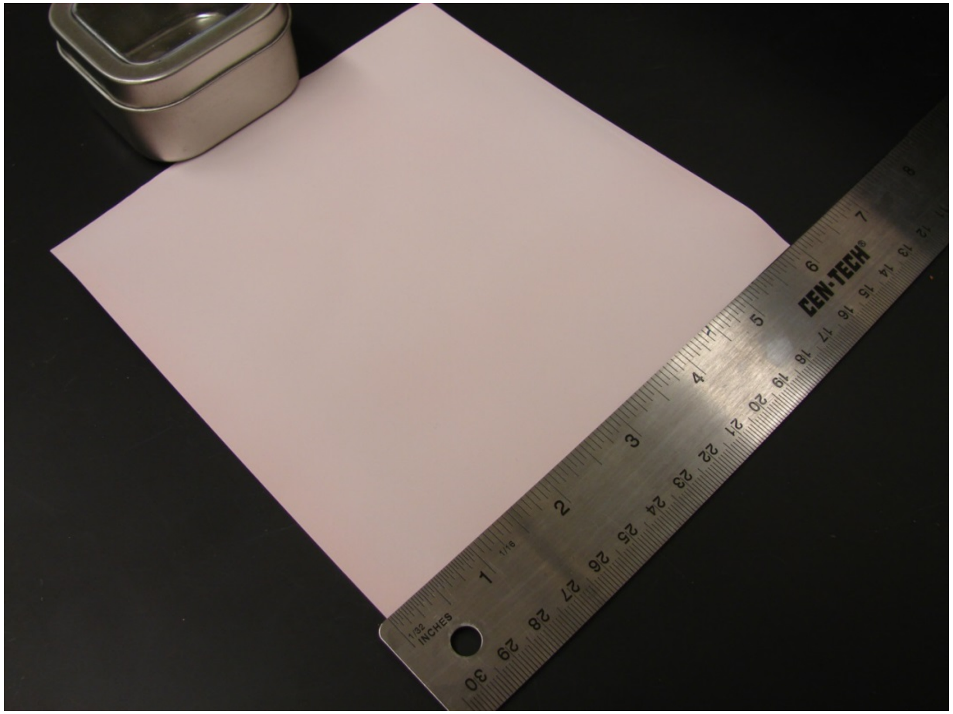


Good quality composites (50 vol.% Ohara ceramic) were formed by spray coating

EARLIER RESULT

- Faster than doctor blade. Air brush good at low viscosity slurry, infinitely scalable.
- On copper, C-coated aluminum, and stainless foils.
- Wetting, uniformity improved with TEGDME. Approx. 30-50 µm before pressing.
- Composition 16:1:2 (EO:Li:TEGDME) to be consistent with earlier melt-pressed.
- Techniques for spray and slurry dispersion are important for quality.

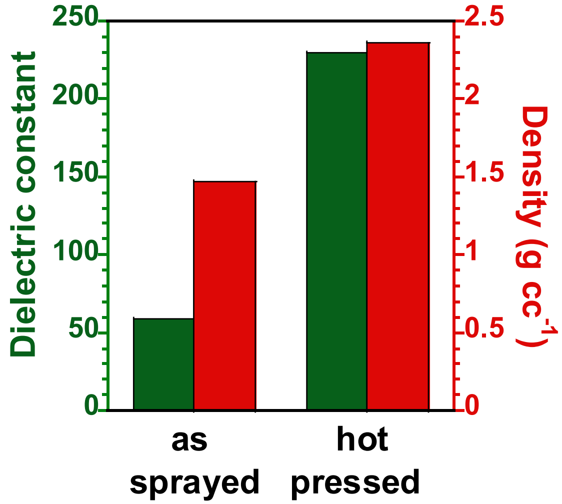




ACCOMPLISHMENT

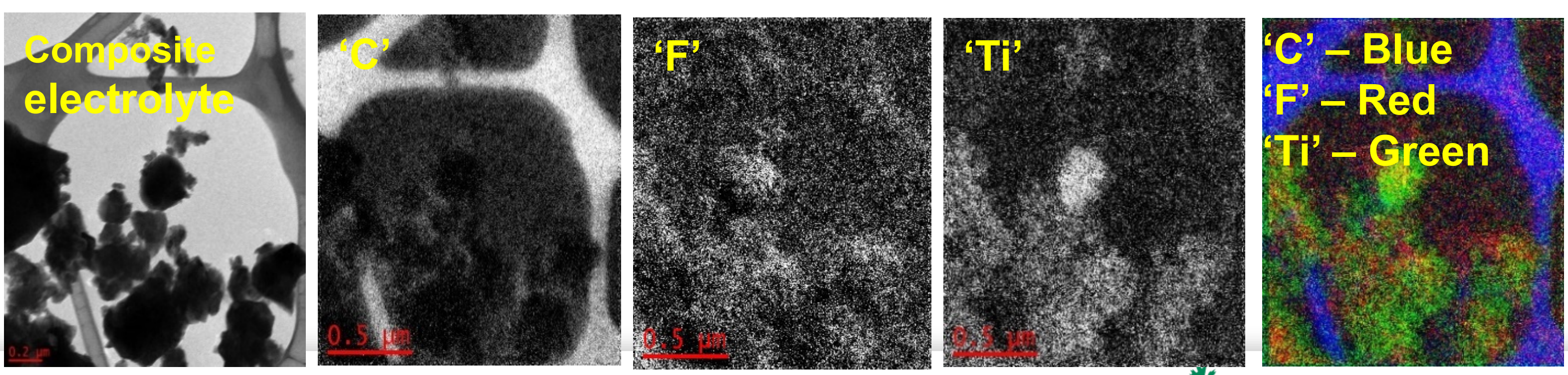
Processing of composites. Spraying – fast and efficient.

- Aqueous slurry, sprayed and dried. All water evaporates, leaving TEGDME which is stable to higher temperatures.
- By EELS-TEM, ceramic powder is well dispersed and coated with PEO+salt.
- Subsequent hot pressing is necessary for higher density and 1000X conductivity.
- Theoretical density and residual porosity are being assessed.



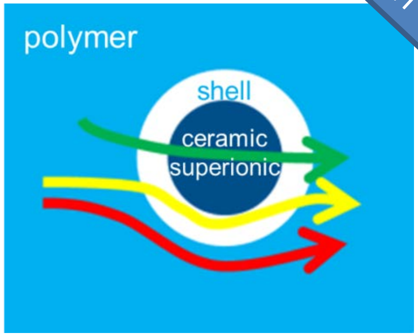
Sample name	Wt % PEO	Wt % LiTFS	Wt % TEGDME	Wt % Ceramic
PE no TEGDME	81.89	18.11	0.00	
PE with TEGDME	54.01	11.95	34.04	
CPE no TEGDME	22.23	4.92	0.00	72.86
CPE with TEGDME	14.66	3.24	9.24	72.86

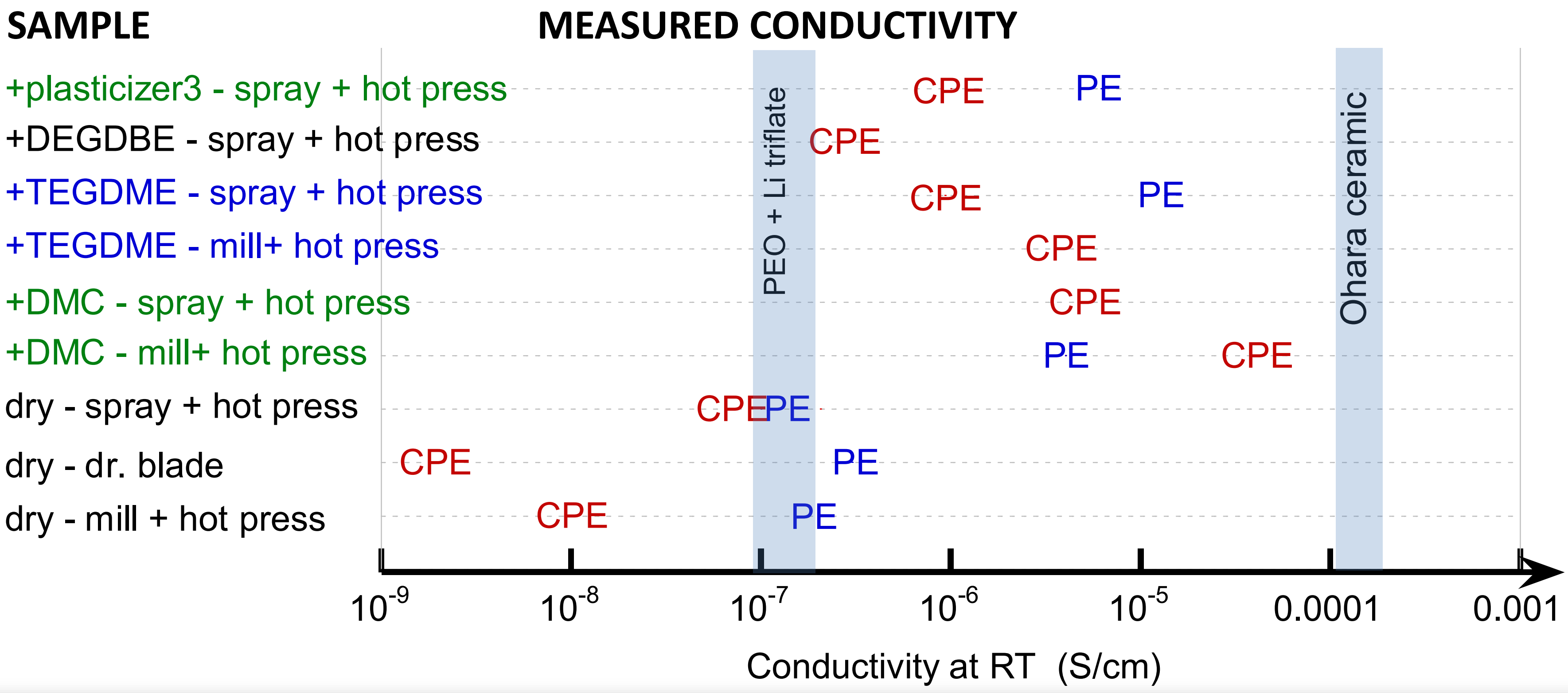
TEGDME:PEO ratio is high. $EO_{PEO}:EO_{TEGDME} = 16:10$



Composites of 40-50v% ceramic were prepared with several different plasticizers. This is key to enhanced conductivity and Li^{+} ionic path. (milestone)

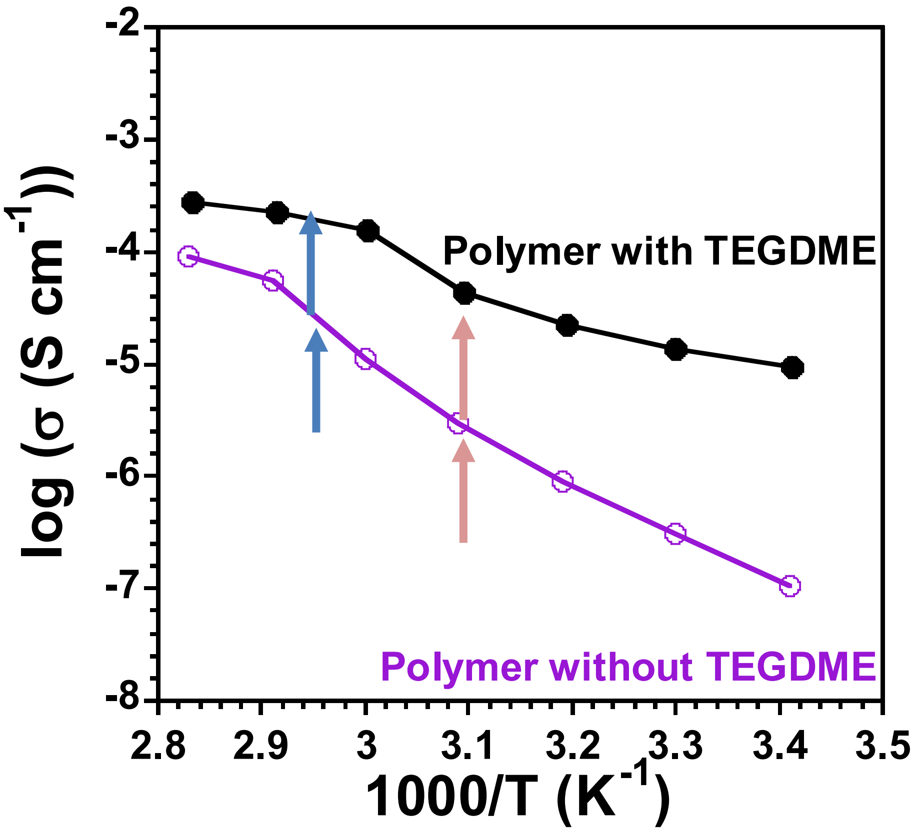
- Only DMC plasticizer provides for participation of ceramic phase. (Composite electrolyte = CPE; Polymer electrolyte=PE)
- Pellets from dry mill and hot pressed powders ≈ coatings from solution spray and hot press or hot roll.

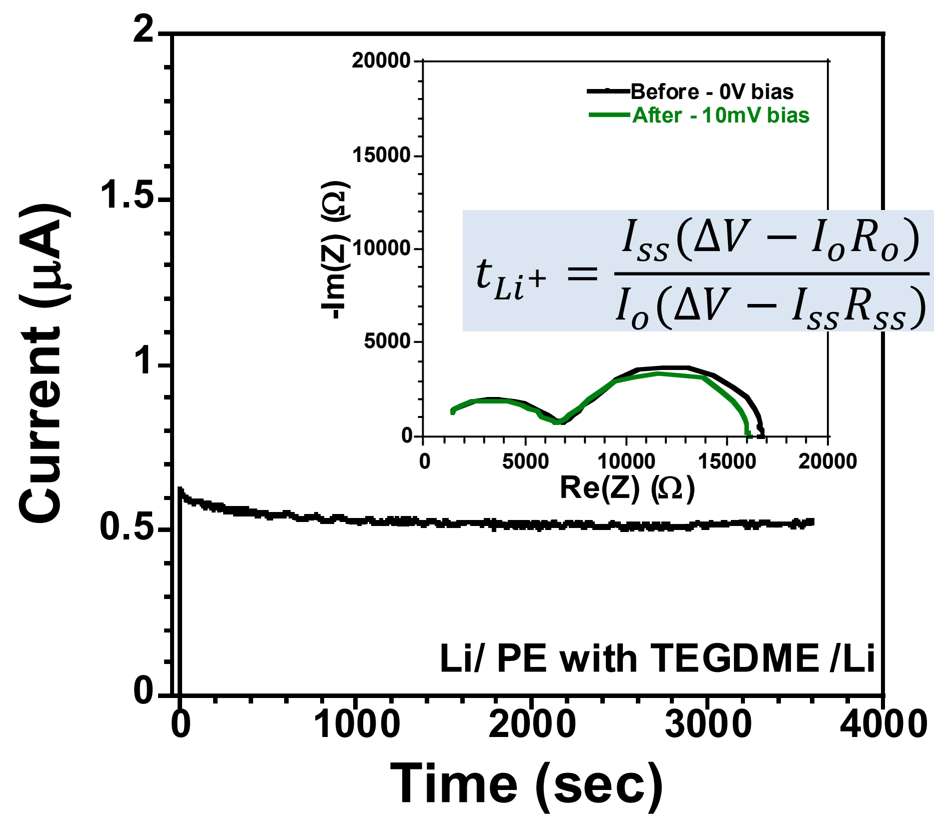




TEGDME (tetraglyme) plasticizes PEO + Li triflate, enhancing the ionic conductivity and membrane quality. (milestone)

- TEGDME, included in the aqueous PEO+salt solution, enhances Li^+ conductivity.
- By DSC, T_c and T_g change by <2°C with TEGDME; T_m by only 0.3°C.
- PE is stable with Li. High interface ASR (~10kΩ) with Li disks pressed to surfaces.
- Transference no. for Li^+ is 0.64 from 1 hr polarization of Li//Li cell. (0.56 without TEGDME, from literature.)





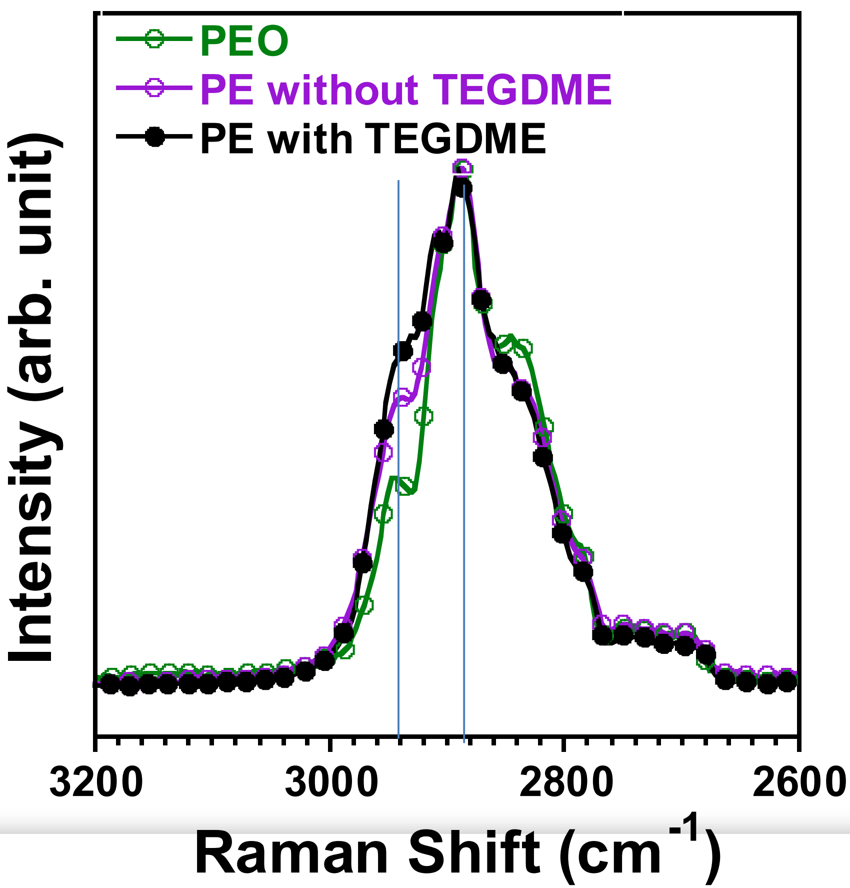
$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_o R_o)}{I_o(\Delta V - I_{ss} R_{ss})}$$

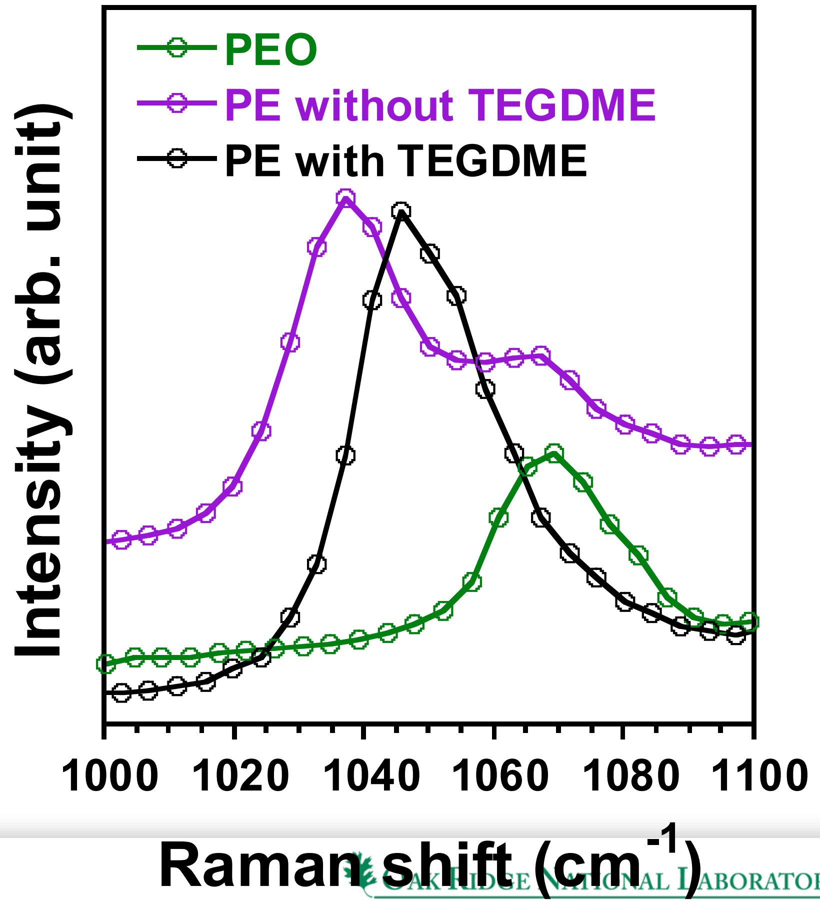
TEGDME (tetraglyme) plasticizes PEO + Li triflate, enhancing the ionic conductivity and membrane quality.

ACCOMPLISHMENT

- Raman study show that TEGDME reduces the volume of crystalline PEO.
  - Ratio I_{2945}/I_{2890} and vol of amorphous PEO increases with salt and TEGDME.
  - Peak at 1045 cm^{-1} Li triflate dissolved in amorphous PEO.

(PE is polymer electrolyte; PEO no salt added)

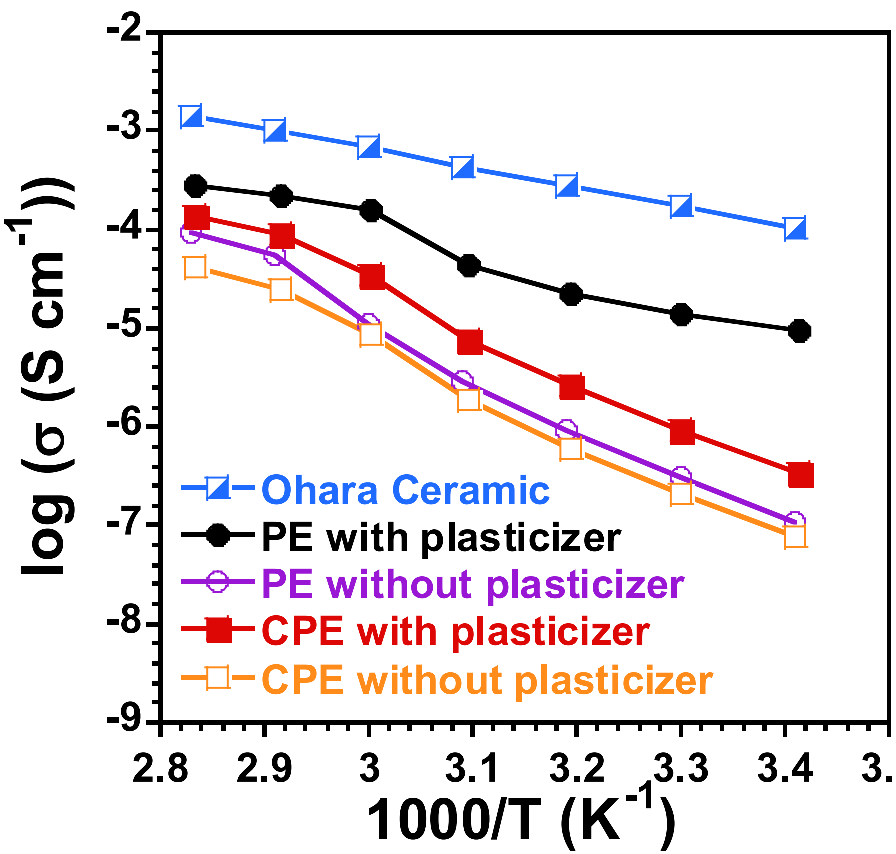


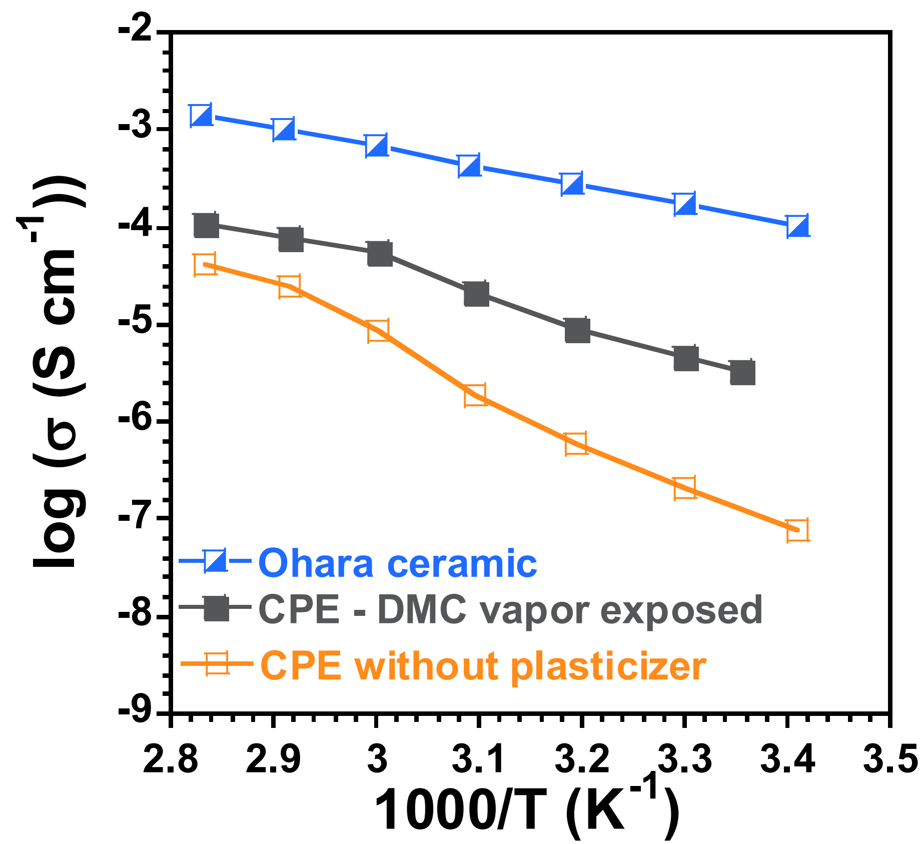


Addition of dispersed ceramic powder (~50 vol%) *reduces* the ionic conductivity for most polymer electrolytes. One exception.

ACCOMPLISHMENT

- Small reduction if no TEGDME (○→□), large reduction if plasticized (●→■).
- Ceramic complicates the FTIR and Raman analysis.
- Assume shell around ceramic particles is resistive.
- But DMC added by vapor treatment has higher conductivity.

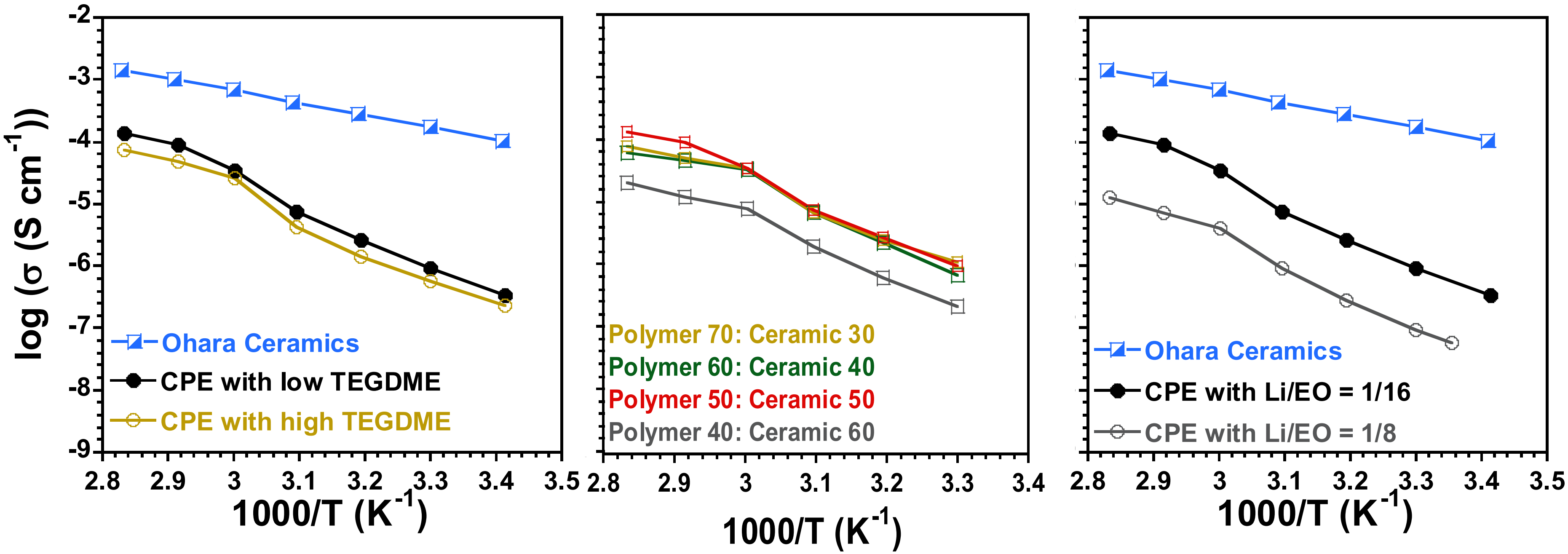




Variations in salt and plasticizer concentrations, as well as the ceramic loading had negative or little impact. (milestone)

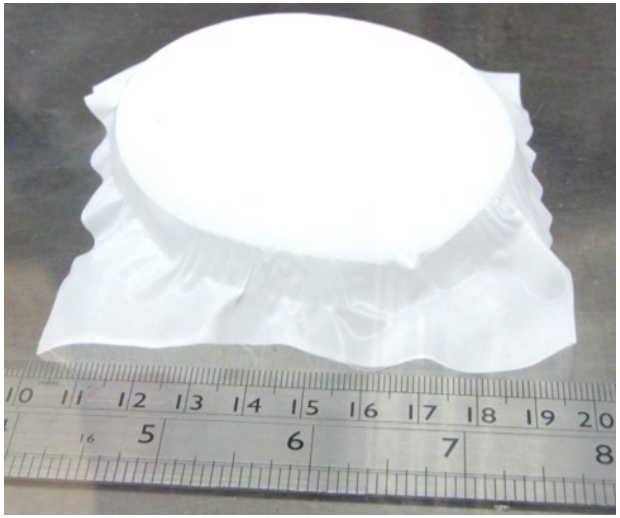
ACCOMPLISHMENT

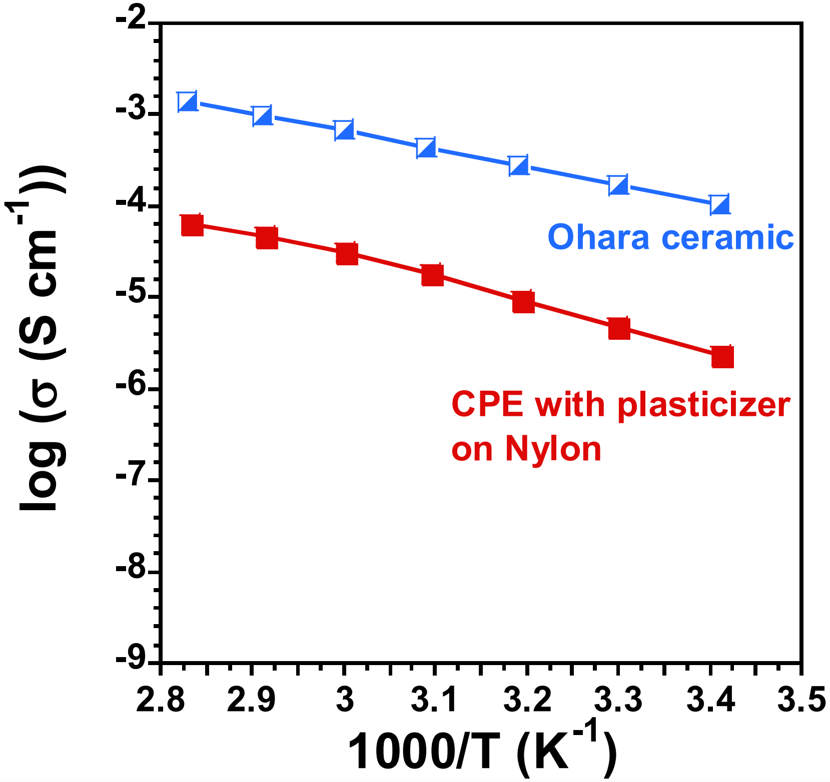
- Plots show examples.
- For reference:
  - Base composition (mole ratio) = 16 PEO + 1 Li triflate + 2 TEGDME
  - Base composition (mole ratio) = 16 C_2H_4O + 1 $LiSO_3CF_3$+ 2 $C_{10}H_{22}O_5$
  - Ceramic powder (base ratio) = 50 vol% (based on PEO and Ohara densities)



Composite with TEGDME and Ohara powder appears to be stable with Li. Also mechanically robust.

- Self supporting CPE membrane is formed by spraying both sides of nylon mesh, and hot pressing.
- EIS measured between stainless electrodes. As the conductivity is higher than for coating on copper, perhaps the mesh has some residual water.
- Next slide shows polarization study with Li contacts.





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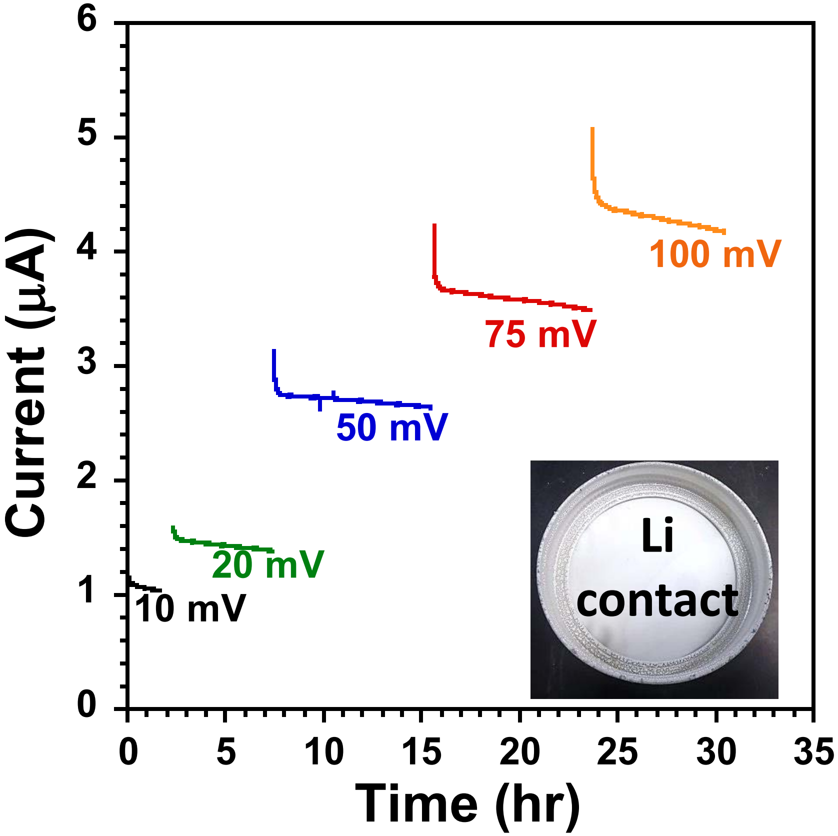
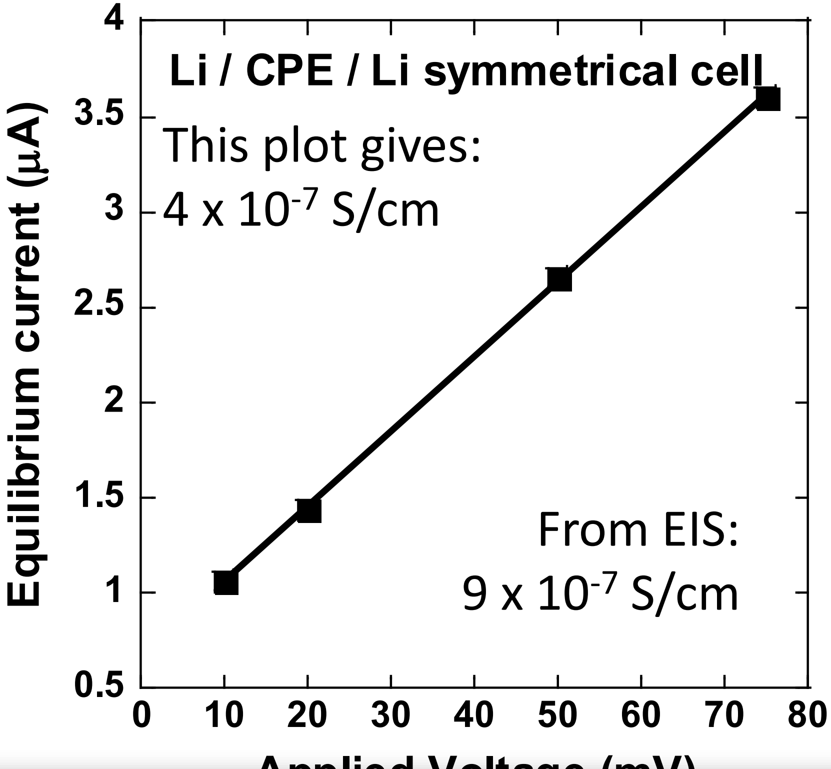
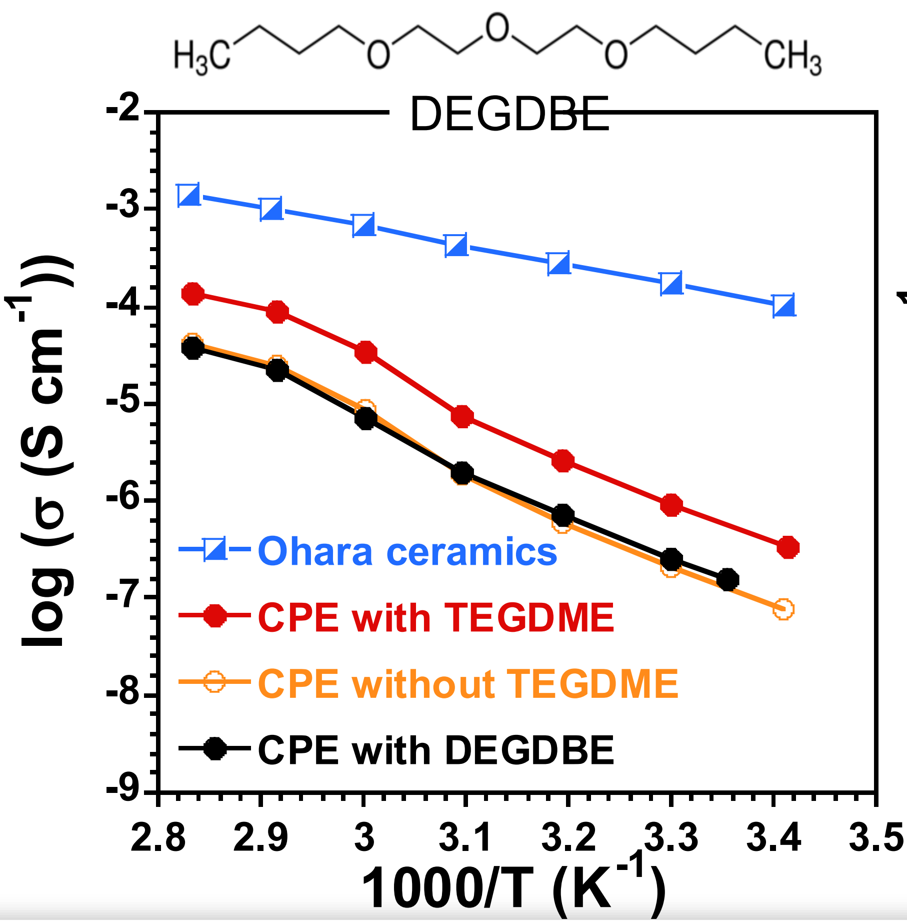


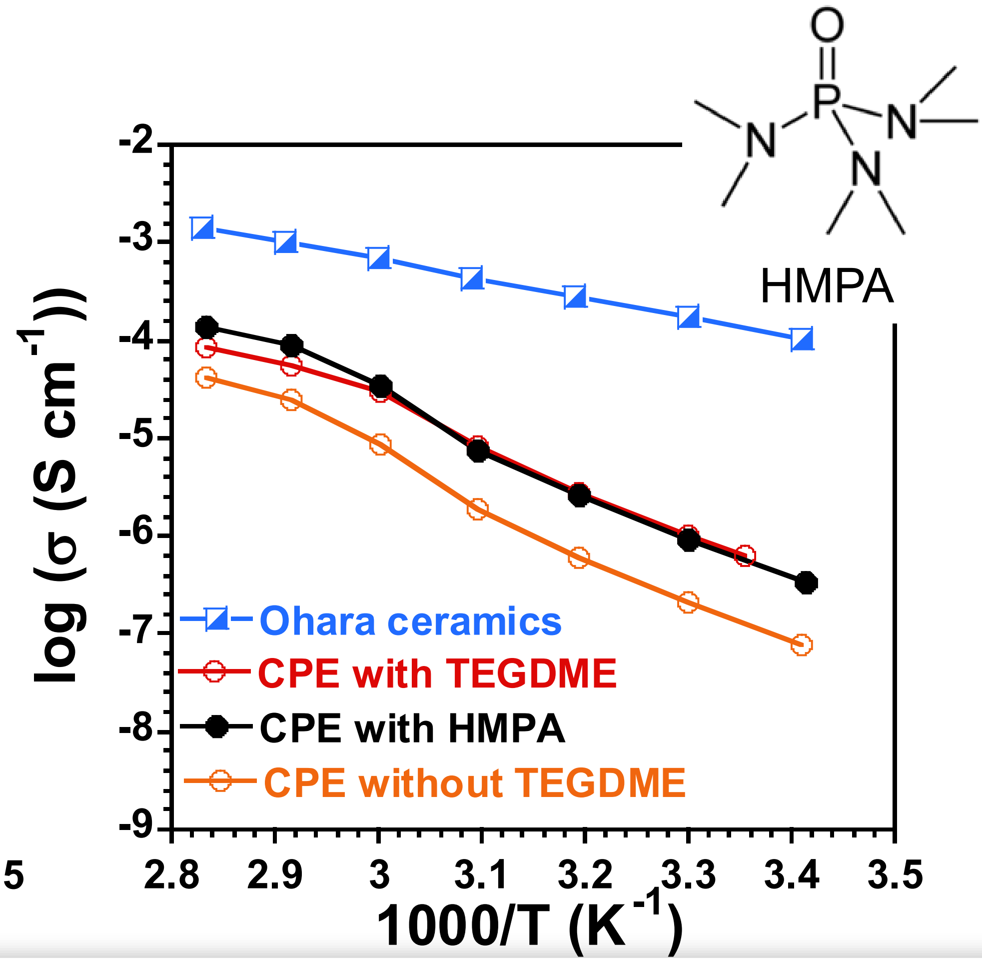


ACCOMPLISHMENT

Other plasticizers have been investigated, but usually CPE has lower conductivity than PE without ceramic.

- Diethylene glycol dibutyl ether has fewer ether oxygens, so expected to reduce solvation of Li^+ → no enhanced conductivity.
- HMPA polar aprotic molecule → comparable to TEGDME. Is it stable with Li?



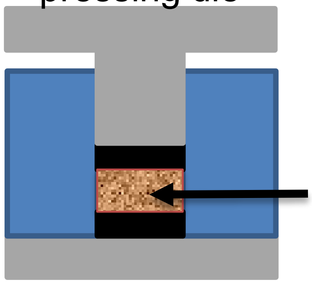


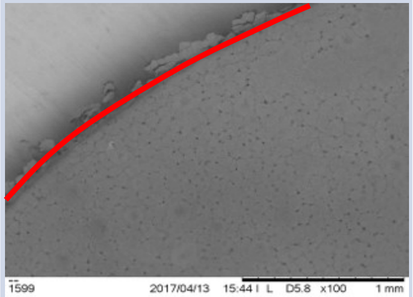
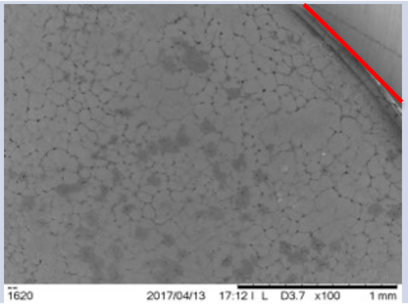
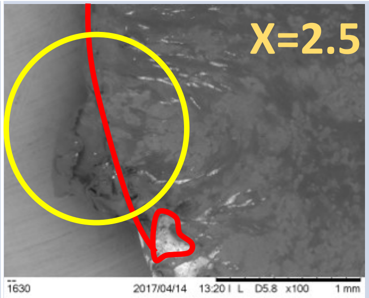
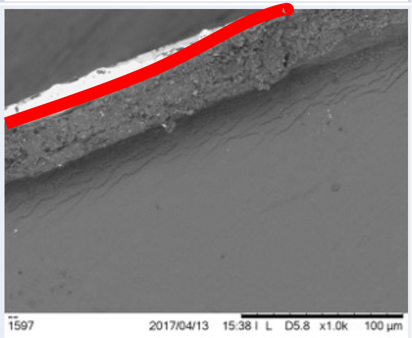
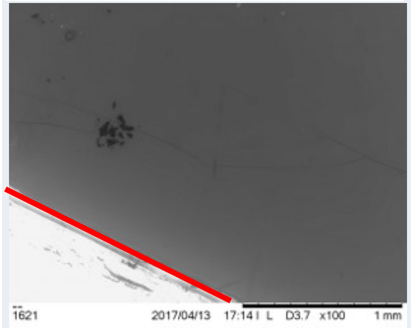
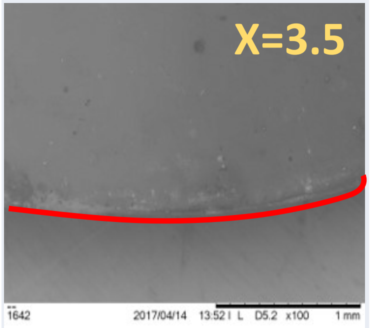
ACCOMPLISHMENT

Lipon sputtered on CPE and PE does not crack under uniaxial load. This coating might be needed to stop Li dendrites.

(milestone)

- Electrolyte with Lipon as top layer withstood at least 1.5 ton/cm^2 for PE and 3.5 ton/cm^2 for CPE.
- Presence of ceramic in CPE delivered a smooth, flat surface for Lipon coating.



Electrolyte sample	As-prepared	After 1.5 ton/cm^2	After X(=max load) ton/cm^2	Remark
PE with TEGDME + LiPON				(RED line = Cu substrate) At max load, PE sample oozed out(YELLOW circle) revealing Cu substrate beneath.
CPE with TEGDME + LiPON				(RED line = Cu substrate) Surface of the sample looked smooth with-out cracks at the center of sample. Sample thickness does not change after testing.

Future Work

FUTURE WORK

Remainder of FY17

- Ion transport in composite polymer electrolyte.
  - Study the EIS of bi- or trilayer samples of spray coated polymer electrolyte over Ohara plates to confirm how TEGDME, DEGDBE and other plasticizers effect the interface transport. Treat the ceramic surface to reduce resistance.
  - With Li contacts, test the transference number and stability of plasticizers with Li.
- Li interface with composite electrolyte.
  - Study the barrier layer (Lipon) over CPE to stabilize the plasticizer and provide for low interface impedance from vapor or melt deposited lithium.
- Full battery by spray coating – fabricate and cycle at or above room temperature.
  - Li-free design built on copper foil with composite cathode sprayed over the composite electrolyte membrane.

Beginning in FY18

- Move beyond model materials used to date with Li stable ceramic and improved polymer to replace PEO.
- Push to higher ceramic loading with bimodal particle sizes. Evaluate mechanical properties.

"Any proposed future work is subject to change based on funding levels."

Challenges and mitigation

- TEGDME is stable with bulk Li contacts, yet may decompose during vacuum Li film deposition. A barrier coating or alternative processing (adding plasticizer after Li deposition) may be solutions.
- A thin electrolyte coating between the composite electrolyte and Li metal will likely be needed for uniform Li plating as well as passivation.
- Having a high ceramic loading is critical to high modulus and high conductivity, but makes processing of very dense membranes more difficult due to particle jamming effects. Bimodal particle size distribution and cold sintering before infusing polymer electrolyte are additional ways to process the composite.

Collaborations and coordination

- Jihua Chen and Bradley S. Lokitz in Soft Materials Program of CNMS, ORNL helped in TEM imaging and obtaining thermal properties using DSC.
- Sakamoto (es277) provides LLZO materials and guidance for air/water reactions.
- Nanda (es106) collaborates on interpretation of Raman characterization.
- Coordination with a BES program at ORNL is synergistic towards understanding synthesis challenges of related solid electrolytes.
- Ceramic electrolytes are supplied by Ohara Corp.

Response to reviewer comments

- No comments were received from poster presentation AMR2016.

Summary

Relevance Success of composite electrolyte will isolate the anode from liquid electrolyte, enabling high energy, thousands of cycles, negligible consumption of lithium, and safety.

Approach

- New approach uses slurry with inexpensive solvent and spray coating to obtain large area of uniform composite films with high ceramic loading.
- Investigate the effect of plasticizer in improving the ionic conductivity and the compatibility with Li electrodes.

Technical accomplishments

- TEGDME plasticizes the PEO electrolyte: reducing the crystallinity and achieving 10^{-5} S/cm, t_{Li+} >0.6, and stability with Li.
- Composites prepared from spray coating aqueous slurries are highly dispersed and uniform. Post processing produces high density, even for 50-60 vol% ceramic loading.
- Composites plasticized with TEGDME are stable with Li, but are too resistive. Similar results were obtained for other candidate Li-stable plasticizer molecules.
- Composites support a compressive load and glassy interface coating.

Future work

- Extend the work with different plasticizers and surface treatment of the ceramic to support ionic conduction as well as compatible with lithium.
- Quantify the ceramic/polymer interface using bi- or tri-layer samples.
- Demonstrate full battery using spray coated cathodes with composite membrane.

Collaborations and coordination – key Sakamoto, Ohara, polymer researchers at ORNL.